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14. ABSTRACT
A research program to study the oxidation chemistry of xylenes at high pressures has been conducted at Drexel University. The current program was initiated in August 2007 through an STIR grant from the Army Research Office (Grant No. W9111NF-07-1-0522, Proposal No. 53267-EG-II) and was completed in May 2008. The objectives of this project were to determine the relative reactivity of the xylene isomers at preignition and autoignition conditions, to study the difference in the isomers in JP-8 surrogates, and to isolate the key xylene oxidation reaction pathways for kinetic model development. The xylenes were oxidized neat, in blends with paraffins, and in JP-8 surrogates in a pressurized flow reactor, with complimentary

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Preignition Chemistry of Xylenes and Their Effect on JP-8 Surrogates

ABSTRACT

A research program to study the oxidation chemistry of xylenes at high pressures has been conducted at Drexel University. The current program was initiated in August 2007 through an STIR grant from the Army Research Office (Grant No. W9111NF-07-1-0522, Proposal No. 53267-EG-II) and was completed in May 2008. The objectives of this project were to determine the relative reactivity of the xylene isomers at preignition and autoignition conditions, to study the difference in the isomers in JP-8 surrogates, and to isolate the key xylene oxidation reaction pathways for kinetic model development. The xylenes were oxidized neat, in blends with paraffins, and in JP-8 surrogates in a pressurized flow reactor, with complimentary experiments conducted in a single cylinder research engine. Detailed kinetic information was obtained utilizing gas chromatography with flame ionization detection and coupling to a mass spectrometer. Several xylene chemical kinetic models were evaluated under the experimental conditions and sensitivity analysis was conducted to compare the modeling predictions' pathways to the experimental results.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Cernansky, N.P., D.L. Miller, R.H. Natelson, and M.S. Kurman. "Preignition Oxidation Chemistry of Xylene." A tribute book for Professor Eliseo Ranzi, Italian Chemical Engineering Society, June 2008.

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(c) Presentations

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Natelson, R.H., R.O. Johnson, M.S. Kurman, N.P. Cernansky, and D.L. Miller. "Preignition and Autoignition Behavior of the Xylene Isomers." Paper No. WSSCI-08S-12, Spring Technical Meeting of the Western States Section of the Combustion Institute, Los Angeles, California, March 17-18, 2008.

Natelson, R.H., M.S. Kurman, D.L. Miller, and N.P. Cernansky. "Oxidation of Alternative Jet Fuels and their Surrogate Components." Paper No. AIAA-2008-970, 46th AIAA Aerospace Sciences Meeting and Exhibit, Reno, Nevada, January 7-10, 2008.

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Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Matthew Kurman	0.50
Rodney Johnson	0.05
Robert Natelson	0.50
FTE Equivalent:	**1.05**
Total Number:	**3**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Nicholas Cernansky	0.03	No
David Miller	0.03	No
FTE Equivalent:	**0.06**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
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NAME
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Names of personnel receiving PHDs

NAME

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Preignition Chemistry of Xylenes and Their Effect on JP-8 Surrogates

FINAL PROGRESS REPORT – TECHNICAL DETAILS

N.P. Cernansky and D.L. Miller

June 2008

U.S. Army Research Office

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12 August 2007 – 12 May 2008

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I. FOREWORD

A research program to study the relative preignition and autoignition reactivity of the xylene isomers has been conducted at Drexel University. The current program was initiated in August 2007 through a grant from the U.S. Army Research Office (Grant No. W911NF-07-1-0522, Proposal No. 53267-EG-II) and was completed in May 2008. The principal objectives were to (1) evaluate the oxidation of the xylene isomers (neat, or, if not reactive neat, with a reactive species to initiate reactivity) in the low and intermediate temperature ranges (typically 600 - 850 K) at elevated pressure (typically 8 atm) in our Pressurized Flow Reactor (PFR), (2) compare the relative reactivity of the xylene isomers as components of possible JP-8 surrogates, (3) perform complimentary autoignition experiments in our single cylinder research engine as appropriate, and (4) conduct a mechanistic analysis study of the experimental data to elucidate the key low and intermediate temperature branching pathways of the xylene isomers.

Experiments were conducted in the PFR facility at Drexel University at temperatures of 600 – 850 K and an elevated pressure of 8 atm. All experiments were conducted at lean equivalence ratios, similar to diesel engines and advanced engine concepts. The design of the PFR allows for the study of fuel preignition oxidation chemistry, without considering the additional complexities of fluid mechanics and temperature gradients. Online analysis of the data included CO and CO_2 measurements using a nondispersive infrared analyzer. During this project, an electrochemical oxygen measuring cell was acquired and utilized for online O_2 measurements. Offline analysis, for identification and quantification of intermediate species, was performed using gas chromatography with flame ionization detection and coupling to a mass spectrometer. Additional experiments were conducted in a single cylinder research engine.

Neat o- and m-xylene were oxidized in the PFR under preignition conditions. They showed no reactivity, so mixtures of each isomer with n-dodecane were tested and compared, and intermediate species were identified. This data helped resolve a recent controversy regarding the relative reactivity of the xylene isomers. Additionally, a mixture of p-xylene/n-dodecane was studied. To study the autoignition of the xylenes, the isomers neat, in binary mixtures with n-decane, and in six-component JP-8 surrogates were tested in the single cylinder research engine. The experimental data were analyzed and compared to existing chemical kinetic models, and it was concluded that at lower temperatures (<840 K), the xylenes show similar reactivity, and at higher temperatures, o-xylene is the slightly more reactive isomer. The data can be used for the improvement of xylene chemical kinetic models, and the conclusions from this study will aid in the selection of the appropriate xylene isomer for JP-8 surrogate fuels.

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III. PROBLEM STATEMENT

This project was motivated by the work of Holley et al. (2007) and Seshadri (2006), which revealed conflicting evidence concerning the relative reactivity of o-xylene (1,2-dimethylbenzene) and m-xylene (1,3-dimethylbenzene) as components of the Violi et al. (2002) JP-8 surrogate in counterflow flame burner ignition and extinction experiments. m-Xylene appeared more reactive, and this conflicted with previous understanding of the xylenes, which was based on neat xylene experiments and showed that o-xylene was more reactive (Lovell et al., 1934; Jackson, 1951; Wright, 1960; Emdee et al., 1990&1991; Roubaud et al., 2000). Considering that xylenes are significant components of real fuels (Guibet, 1999), it is necessary to understand their reactivity for the development of JP-8 surrogates. The development of surrogates, mixtures of 1-10 components that mimic the behavior and properties of real fuels, and their associated chemical kinetic models will provide a powerful means for simulating fuel combustion in engine models, so that advanced engines can be optimized for fuel economy, power output, emissions, and fuel flexibility. Therefore, the first task of this project was to compare the relative reactivity of o- and m-xylene in our PFR facility. The reactivity of hydrocarbons at low and intermediate temperatures is best indicated by the production of carbon monoxide (CO) (Wilk et al., 1989). Additionally, stable intermediate products can be identified and compared among the isomers. The second task was to compare the isomers in JP-8 surrogates. The third task was to conduct complimentary autoignition experiments in our research engine facility. The engine facility operates under a PCI (premixed compression ignition) mode and the reactivity of fuels is monitored with in-cylinder pressure measurements throughout the engine cycle. Using the data acquired from the first three tasks, the last task was to elucidate the key low and intermediate temperature branching pathways of the xylene isomers. To aid in this work, conclusions can be compared to previous experimental and modeling work of the xylenes, which mostly focused on neat xylenes at high temperatures. Additionally, this was to be performed in conjunction with analyzing the existing xylene chemical kinetic models of Ranzi et al. (2007) and Gail and Dagaut (2007) under the experimental conditions of the current project.

IV. EXPERIMENTAL METHODOLOGY

The primary test facility in this program was the Pressurized Flow Reactor (PFR) in the Combustion and Fuels Laboratory at Drexel University. The PFR is designed to study the effects of temperature and pressure on the oxidation of hydrocarbon species at temperatures of 600 – 1000 K and pressures of 2 – 20 atm with relative isolation from fluid mechanics and temperature gradients (Koert and Cernansky, 1992). A schematic of the PFR is shown in Fig. 1. Synthetic air, free of contaminants, is formed by mixing high purity nitrogen (purity = 99.9%) and oxygen (purity = 99.994%). The liquid fuel is injected from a syringe pump into a stream of nitrogen. Vaporization in the absence of oxygen reduces the possibility of premature reaction and heat release. This vaporized fuel in nitrogen and the synthetic air enter the reactor through an opposed jet annular mixing nozzle. The mixture then flows into a quartz reaction tube. A water-cooled, glass-lined stainless steel gas sampling probe is moved inside the reaction tube to collect oxidized samples from the reaction zone at selected probe positions, which correspond to specific reaction times. The methodology followed for these experiments is known as controlled cool down (CCD). In CCD experiments, the PFR is preheated to a specified temperature (typically > 800 K) and once the reaction stabilizes, the PFR is cooled at a rate of 2-5 K/min and the sampling probe is moved to produce a constant residence time. During this cool down, CO and CO_2 are continuously monitored and samples can be collected for detailed analysis at any selected temperature to produce a reactivity map of sampled species concentrations as a function of reaction temperature for the experimental residence time. Experimental error of CO is less than 50 ppm. For analysis offline, up to 15 samples can be collected and stored in a multiple loop storage system, which is heated to 463 K in order to prevent condensation of the less volatile components of the sample. Species are then separated and identified using gas chromatography (GC) with flame ionization detection (FID) and with coupling to a mass spectrometer (MS). For separation, the GC used a fused silica capillary column (Supelco Petrocol DH 100 m length, 0.5 μm film thickness, and 0.25 mm OD). For identification, the spectra from the MS are compared with the NIST Version 2.0 database. Table 1 shows the relevant GC and MS operating parameters.

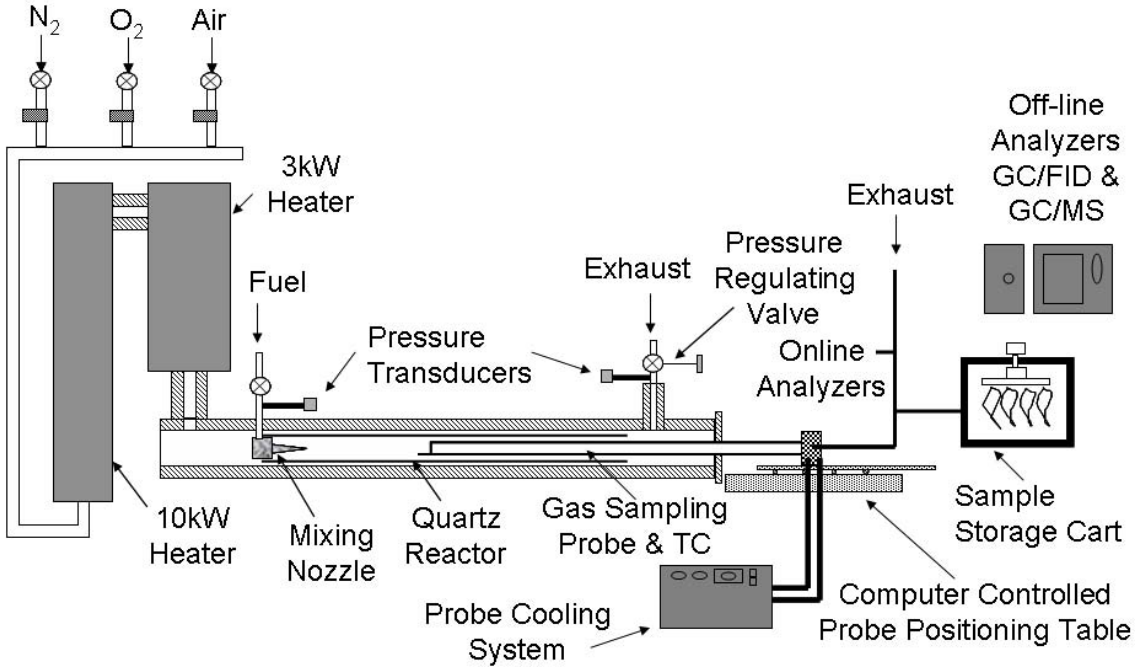

Figure 1: Schematic of the PFR

Table 1: GC/MS/FID Operating Parameters

Gas Chromatograph		**Mass Spectrometer**	
Initial Temperature	-20 °C	Ion Source Temperature	200 °C
Initial Time	5 min	Scan Range	10-250 amu/z
Ramp 1 Rate	10 °C/min	Scan Rate	500 amu/sec
Ramp 1 Temperature	120 °C	Multiplier Voltage	1812 V
Ramp 1 Hold Time	0 min	Ionization Mode	Electron
Ramp 2 Rate	5 °C/min	Electron Energy	-70 eV
Ramp 2 Temperature	250 °C	Emission Current	100 μA
Ramp 2 Hold Time	5 min	Chromatographic Filter	4 sec
Post Analysis Temperature	275 °C		
Post Analysis Pressure	75 psi		
Post Analysis Time	10 min		

Some experiments in support of this program were also carried out in a research engine. The engine facility consists of a single cylinder, Waukesha Motor Corporation Model 48D, Cooperative Fuel Research (CFR) engine directly coupled to a motor dynamometer (Gong, 2005). The engine was operated under a premixed compression ignition (PCI) mode controlled by the autoignition process. A schematic of the engine is shown in Fig. 2. The engine has an 8.26 cm cylinder bore and a variable compression ratio. For our experiments, the compression ratio was set at 16:1, which corresponds to an 11 cm piston stroke and a 589 cm^3 displacement. Also, the inlet manifold pressure was 0.1 MPa and the inlet temperature was 427 K. Test fuel is injected into

the air stream of the heated inlet manifold well upstream of the intake valve to assure complete vaporization and mixing. During a typical experiment, inlet manifold temperature is slowly increased and the reactivity behavior of the fuel is monitored. The autoignition behavior of the fuels is monitored by measuring the in-cylinder pressure with a water-cooled, piezoelectric pressure transducer coupled to a charge amplifier.

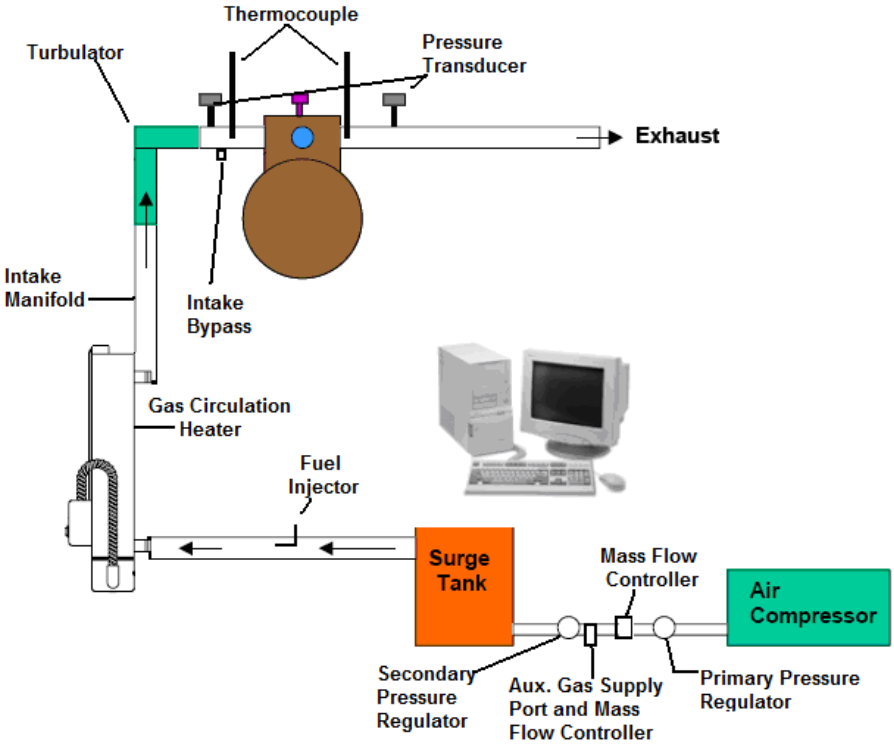

Figure 2: Schematic of the single cylinder research engine

V. SUMMARY OF RESULTS

Several subtasks were completed to achieve the program objectives. The neat xylenes were tested in the PFR and the research engine and showed no reactivity. Thus, binary mixtures of each isomer with a relatively more reactive, previously studied hydrocarbon (n-decane or n-dodecane) were studied. In the PFR, detailed speciation experiments were conducted by collecting 15 samples during each experiment and identifying stable intermediates with GC/MS/FID. In the engine, the relative reactivity of the mixtures was evaluated; additionally, each of the isomers in the Violi et al. (2002) JP-8 surrogate was stressed to autoignition. The Ranzi et al. (2007) chemical kinetic model was evaluated under the conditions of the PFR experiments, and a sensitivity analysis was conducted to elucidate the key low temperature xylene reaction pathways according to the model. These results were compared to a mechanistic analysis study of the key low and intermediate temperature xylene reaction pathways according to the PFR and engine experiments.

The significant findings from this work can be grouped and listed as follows:

(1) Neat xylene oxidation reactivity behavior:
   (a) The xylene isomers, neat, show no reactivity at lean stoichiometry in the PFR.
   (b) The xylene isomers, neat, show no reactivity at lean stoichiometry in the research engine.
   (c) These experimental findings verify the predictions of the Ranzi et al. (2007) and Gail and Dagaut (2007) models.

(2) Key observations of binary mixtures of xylene isomers with a more reactive component:
   (a) Concerning preignition behavior, the xylenes are reactive, but their reactivity is similar such that the isomers can be lumped for chemical kinetic modeling.
   (b) At autoignition conditions, the xylenes are reactive, but o-xylene is slightly more reactive than m- or p-xylene.

(3) Key observations of JP-8 surrogate development:
   (a) A mixture of 77% n-dodecane / 23% m-xylene by volume is significantly more reactive than "average" JP-8 in the PFR.
   (b) The Violi et al. (2002) JP-8 surrogate with m-xylene, as originally suggested, matches "average" JP-8 better in the research engine than the surrogate with o-xylene as tested by Seshadri (2006).

(4) Key findings concerning reaction pathways of the xylene isomers from preignition to autoignition:
   (a) When mixed with a reactive paraffin in the PFR at temperatures of 600-840 K, the xylene isomers are reactive, with each isomer producing its respective tolualdehyde isomer and toluene.

(b) When mixed with a reactive paraffin in the research engine and stressed to autoignition, the xylene isomers are reactive, but there are slight differences in reactivity due to the isomeric structure.

(c) The current findings of low temperature xylene reaction intermediates disagree with the key predictions of the Ranzi et al. (2007) model, although the overall general reactivity behavior is predicted and the validity of xylene isomer lumping is confirmed.

Details of the subtasks described above and work leading to the significant findings follow.

A. Neat Xylene Oxidation

To investigate the preignition behavior of neat xylenes in the PFR, neat xylene was oxidized at 0.30 equivalence ratio, 120 ms residence time, 8 atm pressure, and 600-832 K temperatures. The diluted mixture was composed of, in molar fractions, 0.00120 (1200 ppm) xylene (o- and m- separately), 0.957 N_2, and 0.0420 O_2. CO and CO_2 were monitored and not produced, indicating that the neat fuel was not reactive. Furthermore, an electrochemical oxygen measuring cell was acquired and installed during the course of the project for online measuring of O_2. Additional experiments were conducted and no significant reduction in O_2 was observed, further confirming the non-reactive nature of the neat xylenes under these test conditions.

Complimentary experiments were conducted in the research engine. To simulate conditions similar to PCI engines at low loads, tests were run at lean mixtures (0.26 equivalence ratio) and low engine speed (750 RPM). A motored run with no fuel was performed, as well as neat runs for o-, m-, and p-xylene. The in-cylinder pressure rises for the neat xylene runs during the engine cycle matched the motored run, indicating no sign of energy release or reactivity.

An existing chemical kinetic model (310 species, 8011 reactions) with the associated thermodynamics file was generously supplied by Ranzi et al. (2007) and evaluated for the PFR conditions. The model is a semi-detailed mechanism of the pyrolysis, partial oxidation, and combustion of hydrocarbon fuels up to C_{16} and is applicable for low and high temperatures. It should be noted that in the model the three xylene isomers are not differentiated, typical “lumped” analysis. The model was evaluated in Chemkin 4.1 (Kee et al., 2006) and, to match our reactor, the Plug Flow Reactor subroutine, under isothermal conditions, was used with calculations for a reactor length of 40 cm. Simulating the neat xylene experiments in the PFR, the model predicted no reactivity, corresponding with the experimental results.

Additionally, the m-xylene chemical kinetic of Gail and Dagaut (2007) was generously supplied with the associated thermodynamics file. The model is a detailed mechanism (189 species, 1359 reactions) for the combustion of m-xylene and its development was primarily based on the experimental behavior of m-xylene

oxidized in a jet-stirred reactor at high temperatures (900-1400 K). The model was simulated under the PFR experimental conditions and successfully predicted no reactivity.

B. Xylene / Paraffin Mixtures Oxidation

To potentially initiate reactivity of the xylenes, mixtures with more reactive species that would generate an initial radical pool were tested. Compositions of 77% n-dodecane / 23% xylene by volume were selected because the Jet Fuel Surrogate Working Group (2008) recommended a JP-8 surrogate of 77% n-dodecane / 23% m-xylene for modeling soot formation.

Figure 3 shows the results of the PFR experiment with 77% n-dodecane / 23% o-xylene, oxidized at 0.23 equivalence ratio, 110 ms residence time, 8 atm pressure, and 600-837 K temperatures. The diluted mixture was composed of, in molar fractions, 0.00046 (460 ppm) fuel, 0.968 N_2, and 0.0315 O_2. The graph shown is a characteristic "reactivity map." Significant reactivity (>150 ppm CO) was observed at 628 K, and increased with increasing temperature until peak reactivity, 1030 ppm CO, occurred at 699 K. Reactivity then decreased with increasing temperature in the Negative Temperature Coefficient (NTC) region. Significant reactivity was observed until 797 K, and by the maximum temperature of 837 K no CO was produced. CO_2 showed similar trends at approximately 1/3 the production level.

Figure 4 shows the results of the PFR experiment with 77% n-dodecane / 23% m-xylene, oxidized under the same conditions as the aforementioned experiment with o-xylene. The results are similar, with a maximum of 1030 ppm CO produced at 693 K. Figure 5 shows a comparison of the two experiments, indicating more clearly that there is no difference in CO production between m-xylene and o-xylene in the low temperature regime.

Additionally, the oxidation of this mixture was simulated in Chemkin 4.1 using the model of Ranzi et al. (2007). At temperatures up to 665 K, the model predicted CO formation very well, but the peak CO formation was underpredicted, at a significantly lower temperature (670 K) and level (729 ppm). Furthermore, the model predicted the initiation of intermediate temperature reactivity, with CO rising with increasing temperature in the range of 820-840 K. This behavior was not observed in the experiment. Nevertheless, considering that the existing model was not developed with any special consideration for xylene preignition chemistry, and was completely unmodified for this work, the predictions captured the general behavior quite well.

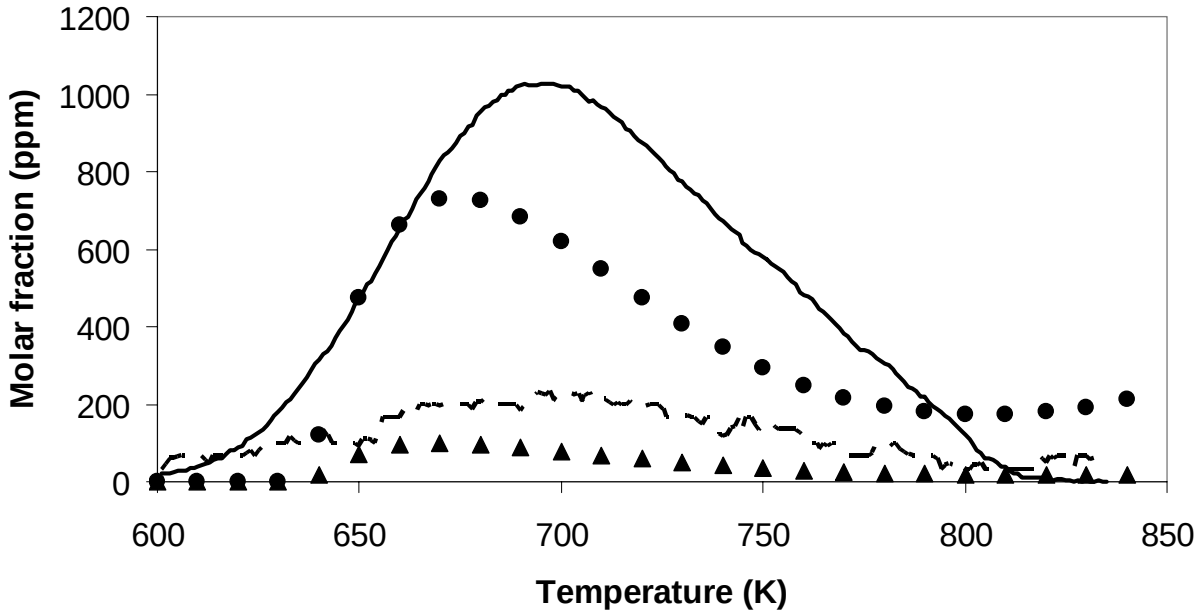

Figure 3: Preignition of 77% n-dodecane / 23% o-xylene in the PFR: (—): CO (experiment), (●): CO (model), (--): CO_2 (experiment), (▲): CO_2 (model).

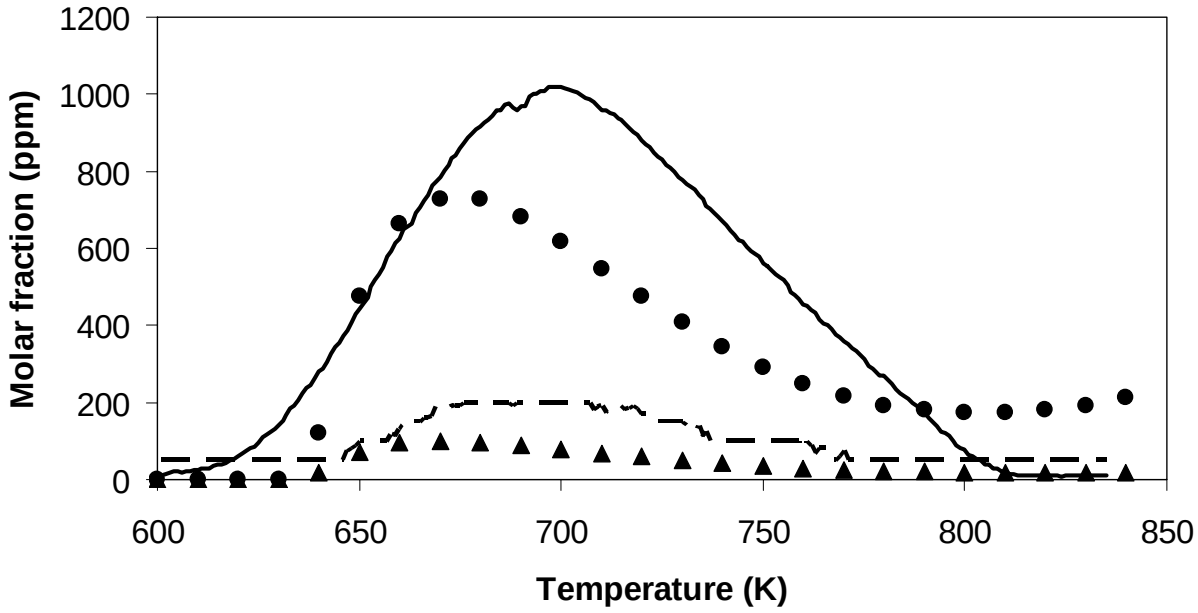

Figure 4: Preignition of 77% n-dodecane / 23% m-xylene in the PFR: (—): CO (experiment), (●): CO (model), (--): CO_2 (experiment), (▲): CO_2 (model).

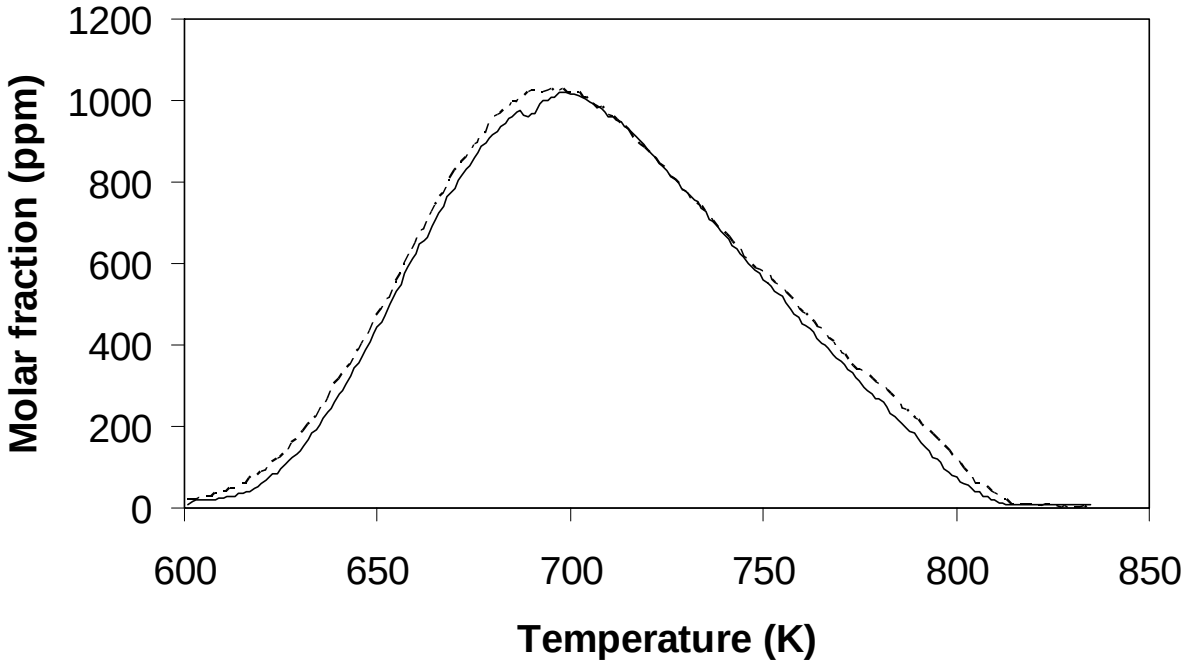

Figure 5: CO production from preignition of 77% n-dodecane / 23% xylene in the PFR: (--): o-xylene, (—): m-xylene.

Intermediate species were collected at 15 temperatures during the n-dodecane / o-xylene experiment in the PFR and analyzed with GC/MS/FID. At 837 K, a sample was collected before O_2 was introduced into the PFR, for fuel calibration purposes and to check for fuel cracking. Only the parent fuels were identified in this sample. After O_2 was introduced, over 30 intermediate species were identified in the remaining samples. Most of them can largely be attributed to n-dodecane oxidation, including linear alkenes (ethene, propene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, and several dodecene isomers), saturated aldehydes (acetaldehyde, propanal, butanal, pentanal, hexanal, and heptanal), unsaturated aldehydes (2-propenal, 2-methyl-2-propenal, and 2-methyl-2-butenal), and ketones (methyl vinyl ketone, 2-butanone, 2-pentanone, and 2-hexanone). These results agree with a previous investigation of n-dodecane oxidation in the PFR (Lenhert, 2004). Several cyclic ethers (2-methylfuran, tetrahydro-2-methylfuran, and 2-butyltetrahydrofuran) were identified in this experiment but not in the previous n-dodecane experiment. However, the GC technique was improved for noise reduction since the previous study so that species with lower concentrations could now be identified, and it was suspected that they were produced from the n-dodecane. Later neat n-dodecane work confirmed this. Nonetheless, aromatic species were identified (o-tolualdehyde and toluene) and attributed to o-xylene oxidation. Table 2 shows the key species relevant for this study, including the parent fuels, and the temperatures where they were identified. The same GC/MS/FID procedure was followed for the m-xylene

experiment, and similar results were found, except that m-tolualdehyde was identified instead of o-tolualdehyde. Table 3 shows the corresponding key species. Again, a sample collected at 834 K before O_2 was introduced showed no fuel pyrolysis.

Table 2: Key species identified from the 77% n-dodecane / 23% o-xylene PFR experiment, temperatures in K.

Species	625	650	670	680	690	705	720	740	760	775	800	805	815	825	837
o-Tolualdehyde	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Toluene	X	X	X	X	X	X	X	X	X	X	X	X	X		
o-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
n-Dodecane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Table 3: Key species identified from the 77% n-dodecane / 23% m-xylene experiment, temperatures in K.

Species	625	650	670	680	690	705	720	740	760	775	800	805	815	825	834
m-Tolualdehyde	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Toluene	X	X	X	X	X	X	X	X	X	X	X	X	X		
m-Xylene	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
n-Dodecane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

A mixture of 77% n-dodecane / 23% p-xylene was also tested in the PFR with GC/MS/FID. Because of low GC peaks in the previous experiments due to low fuel loadings, the p-xylene experiment was run at a higher fuel concentration (800 ppm fuel) and equivalence ratio (0.30). Aromatic intermediate species identified included p-tolualdehyde, toluene, and p-cresol.

To determine the reactivity of xylene in mixtures, experiments were repeated for neat n-dodecane in the PFR under the same conditions (pressure, equivalence ratio, nitrogen dilution, and residence time) as the n-dodecane / (o- and m-) xylene mixtures. Figure 6 compares the CO production of this experiment, with the 77% n-dodecane / 23% m-xylene experiment and the projected results if the m-xylene was not reactive (64% of the CO by mole produced by the neat n-dodecane experiment, since the mixture contains 64% n-dodecane by molar fraction). Neat n-dodecane produced a maximum of 1540 ppm CO at 697 K. The simulation of 77% n-dodecane / 23% non-reactive species produced 990 ppm CO, 40 ppm CO less than the actual results of 77% n-dodecane / 23% m-xylene. It appears that the xylene does not have an effect on the simulated overall reactivity of the mixtures at preignition.

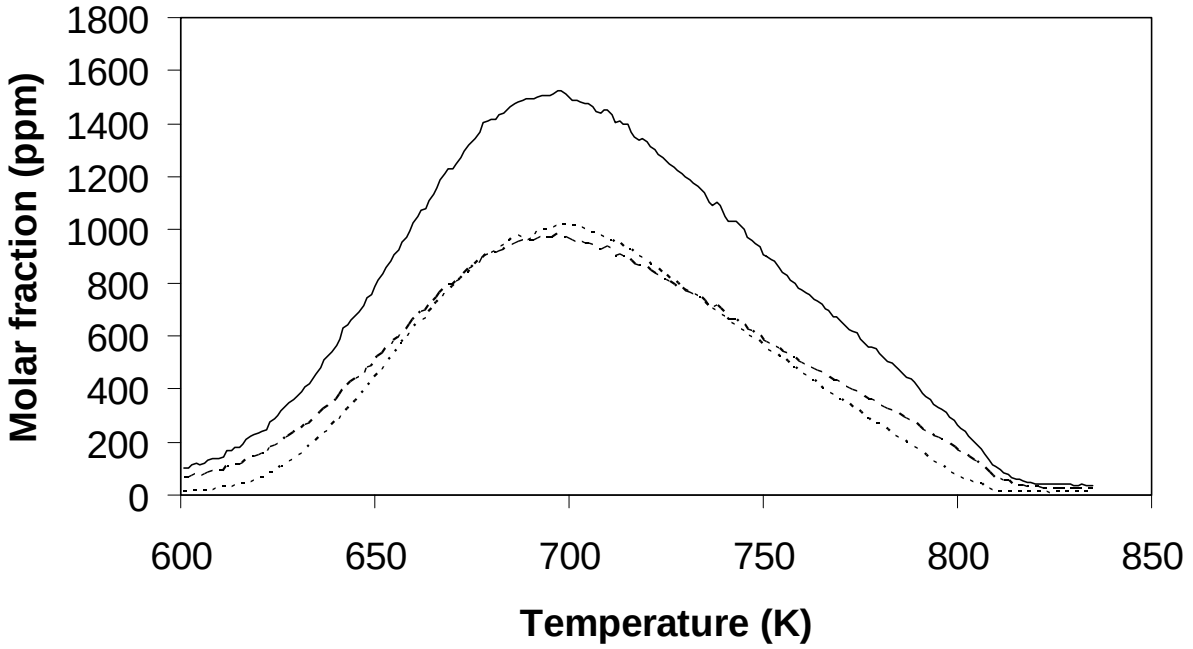

Figure 6: CO production in the PFR: (—): n-dodecane, (--): simulation of 77% n-dodecane / 23% non-reactive species, (…): 77% n-dodecane / 23% m-xylene.

Furthermore, to explore the relative reactivity of the xylene isomers under autoignition conditions, experiments were conducted in the research engine. As these experiments were conducted before the recommendation of the Jet Fuel Surrogate Working Group (2008), the mixture was slightly different, composed of 85% n-decane / 15% xylene. Figure 7 shows data from the autoignition regime of the engine cycle, with emphasis on the portion relevant for this study. The x-axis refers to the crank angle degrees with 360° being top dead center for compression. The onset of combustion is the initial upward bend in the pressure trace. The binary mixtures with p-xylene or m-xylene (first two DX blends) showed combustion onset at 334 CAD. The mixture with o-xylene (third DX blend) reacted slightly sooner, at 333 CAD.

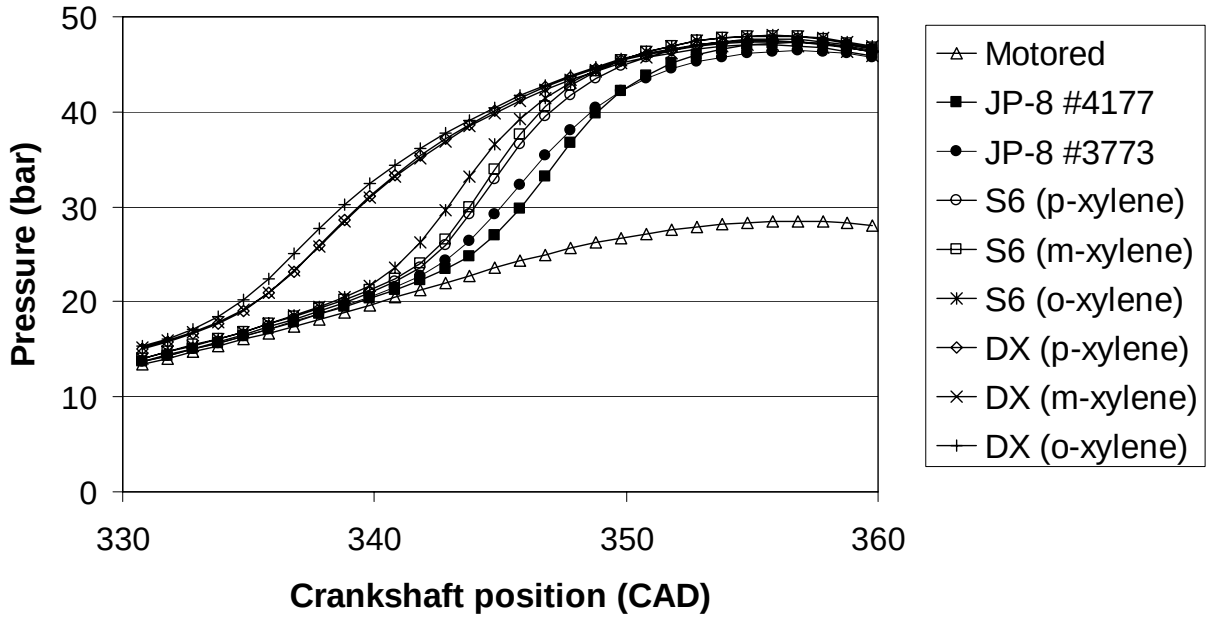

Figure 7: Autoignition of fuels in the single cylinder CFR engine. S6 is the Violi et al. (2002) surrogate, composed of 15% xylene / 10% iso-octane / 20% methylcyclohexane / 30% n-dodecane / 20% n-tetradecane / 5% tetralin. DX is a binary blend composed of 15% xylene / 85% n-decane. DX with p-xylene and m-xylene showed overlapping data. Neat p-xylene, m-xylene, and o-xylene data overlapped with motored run.

C. Xylene Oxidation in JP-8 Surrogates

Since the mixture of 77% n-dodecane / 23% m-xylene mixture was selected based on a recommendation for matching JP-8 soot formation, a sample of JP-8, previously determined to be of "average" reactivity and composition (Natelson et al., 2008), was tested under the same conditions. Figure 8 shows a comparison with the mixture and JP-8. Both experiments were run at 0.23 equivalence ratio, 110 ms residence time, and 8 atm pressure. The JP-8 produced a maximum of 540 ppm CO at 694 K. Thus, the mixture was approximately twice as reactive as the JP-8 under preignition conditions, and would be a poor choice for a surrogate for these conditions. Nevertheless, the surrogate may still be a good choice for matching soot formation, as the sooting phenomenon is a high temperature process. These observations and results highlight the difficulty in developing a single surrogate for all performance criteria.

In the research engine, the six-component Violi et al. (2002) surrogate was tested with each of the xylene isomers (S6 blends). Figure 7 shows the pressure traces, compared to two samples of JP-8, including "average" JP-8, #3773. The surrogate with either m-xylene or p-xylene showed onset of combustion at 341 CAD. However, the surrogate with o-xylene showed slightly different behavior, with combustion onset sooner at 339 CAD. For JP-8 #4177, the onset of combustion occurred at 343 CAD. JP-8 #3773 showed onset of combustion slightly sooner, at 342 CAD. Thus, the original Violi et al. (2002) surrogate with m-xylene matches JP-8 better than the modified Seshadri (2006) surrogate with o-xylene. Considering an uncertainty of ±1.5

CAD, however, it appears that the differences are slight. In practical terms, it appears that the xylenes' reactivity is fairly similar.

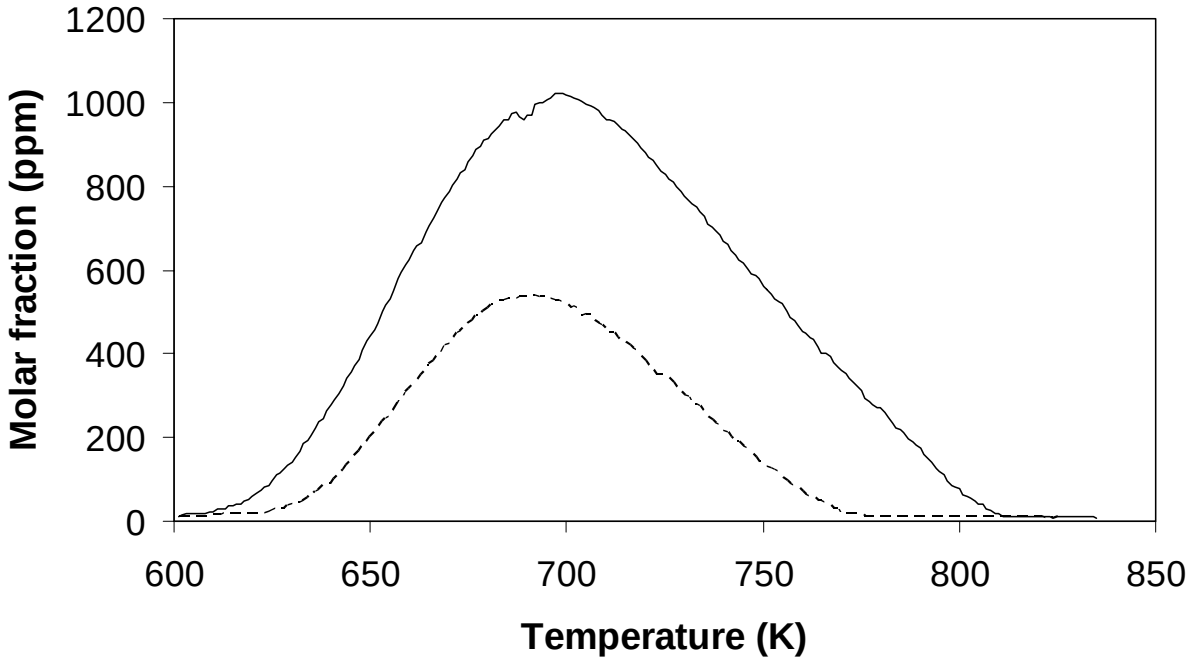

Figure 8: CO production from preignition in the PFR: (—): 77% n-dodecane / 23% m-xylene, (--): JP-8 #3773.

D. Key Xylene Reaction Pathways at Preignition and Autoignition Conditions

The relative reactivity of the xylenes in the PFR and the engine did not completely agree. In the PFR, o- or m-xylene with n-dodecane showed the same reactivity and produced the same intermediate species. However, in the engine, the binary mixture and the six-component JP-8 surrogate showed more reactivity with o-xylene compared to m-xylene or p-xylene as the xylene isomer component. Emdee et al. (1990&1991) identified the major oxidation routes of the isomers and identified the significance in the pathway to xylylene. Hydrogen abstraction from o-xylene produces the o-xylyl radical, and reaction with molecular oxygen produces o-xylylene. o-Xylylene then easily isomerizes to styrene, which can decompose to the reactive species phenyl and vinyl radicals. It is possible that this pathway is not dominant at the preignition temperatures in the PFR, but becomes activated at the higher temperatures in the engine, and thus enables the increased reactivity of o-xylene at high temperatures. This is because the xylylene pathway is dependent upon the isomer. For m-xylene, Pollack et al. (1981) found that m-xylylene has a much higher heat of formation than o-xylylene or p-xylylene, and thus there is no pathway to rapidly lead to the phenyl and vinyl radicals. For p-xylene, Emdee et al. (1991) showed that p-xylylene is produced, but the latter leads to other species maintaining the p-xylene structure rather than the phenyl and vinyl radicals.

At the lower temperatures in PFR, another pathway for the o-xylyl radical may be dominant. This scheme is the production of o-tolualdehyde and an atomic hydrogen radical from the reaction of the o-xylyl radical with an atomic oxygen radical (Emdee et al., 1990). This pathway possibly explains the production of o-tolualdehyde in the n-dodecane / o-xylene PFR experiment. Similar pathways for the production of m-tolualdehyde from m-xylene and p-tolualdehyde from p-xylene are also possible.

Another possible pathway for xylene is the production of toluene. Gail and Dagaut (2007) suggested the reaction of m-xylene and an atomic hydrogen radical to produce toluene and a methyl radical (No. 1182 in their paper), using parameters including a pre-exponential factor (A) of 1.80×10^{14} and an activation energy (E_a) of 8,090 cal/mol. A competing pathway is the reaction of m-xylene and an atomic hydrogen radical to produce an m-xylyl radical and molecular hydrogen. Gail and Dagaut (2007) included this reaction (No. 1177), using an A of 1.00×10^{14} cm^3 / (mol^*K^*s) and an E_a of 8,370 cal/mol. Figure 9 shows the rate constants (k) for these reactions, indicating both are active at lower temperatures with sufficient quantities of atomic hydrogen radicals.

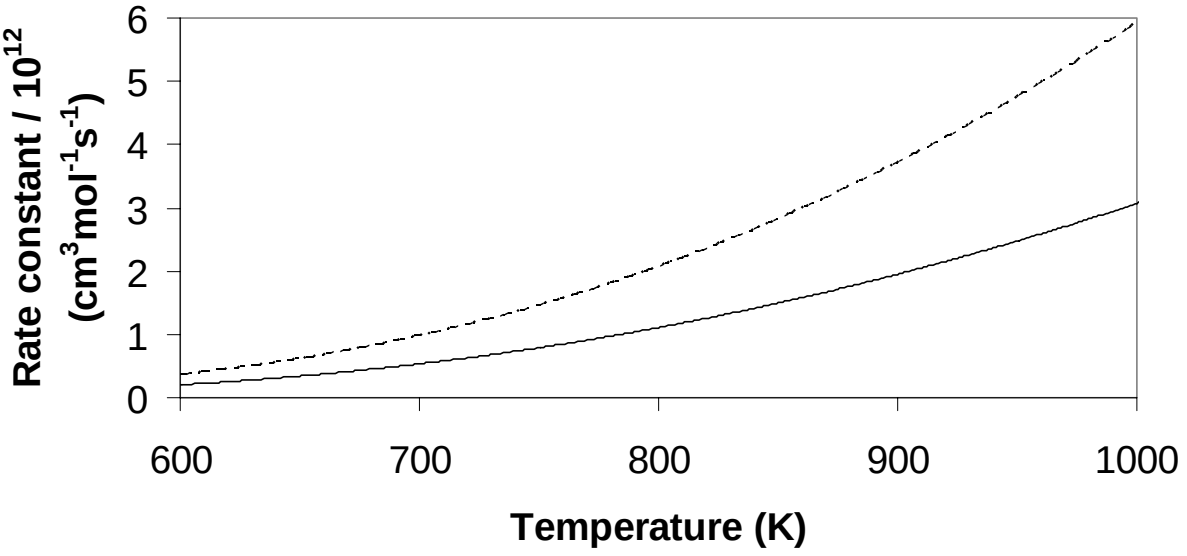

Figure 9: Rate constants of reactions No. 1182 (—) and No. 1177 (--) from Gail and Dagaut (2007).

Based on the experimental findings and previous high temperature xylene work, general schematics of the low temperature oxidation of each of the isomers were developed. Figure 10 shows the pathways of o-xylene oxidation, with the pathway producing the 2-methylbenzyl radical (o-xylyl radical) and then 2-methylbenzaldehyde (o-tolualdehyde) preferred at lower temperatures. At higher temperatures, the o-xylyl radical leads to 5,6-bis(methylene)cyclohexa-1,3-diene (o-xylylene), which isomerizes to styrene. Figure 11

shows the p-xylene oxidation pathways, with the key difference being that 3,6-bis(methylene)cyclohexa-1,4-diene (p-xylylene) leads to other alkylated aromatics maintaining the p-xylene structure. Figure 12 shows the m-xylene oxidation pathways, with the key difference being that the 3-methylbenzyl radical (m-xylyl radical) leads to other alkylated aromatics maintaining the m-xylene structure.

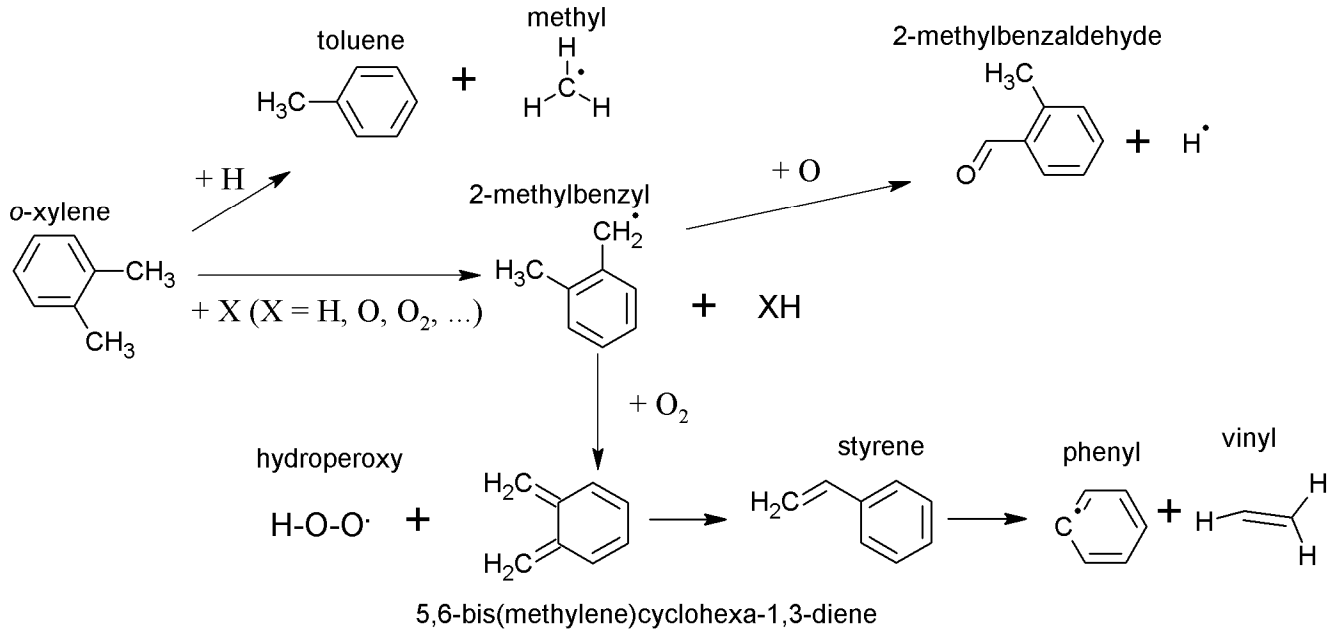

Figure 10: Key branching pathways of o-xylene oxidation.

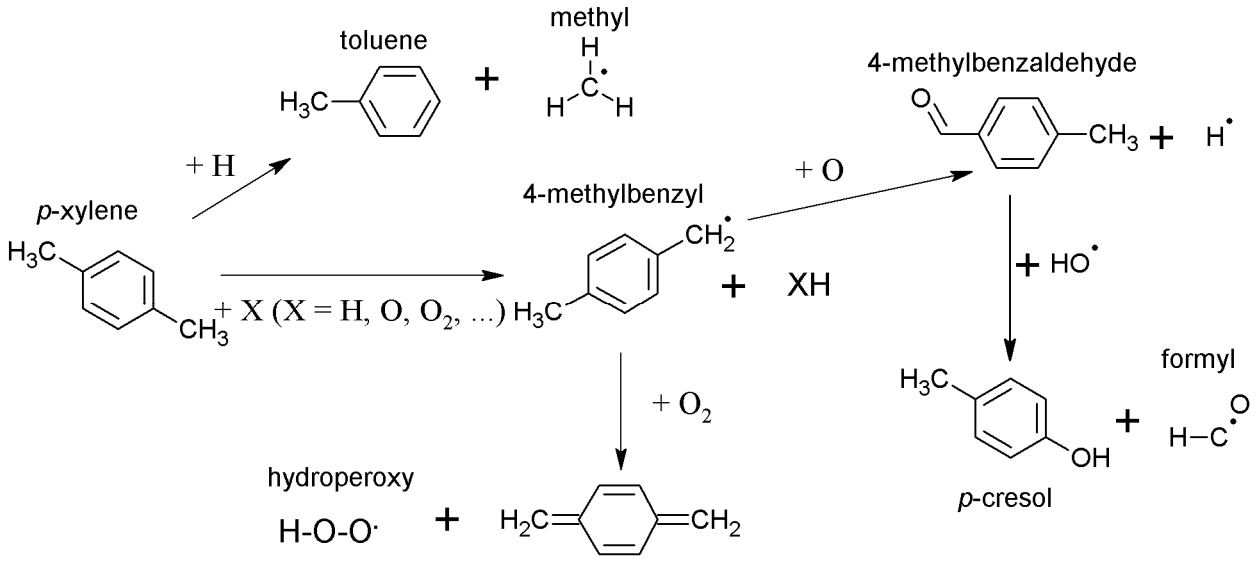

Figure 11: Key branching pathways of p-xylene oxidation.

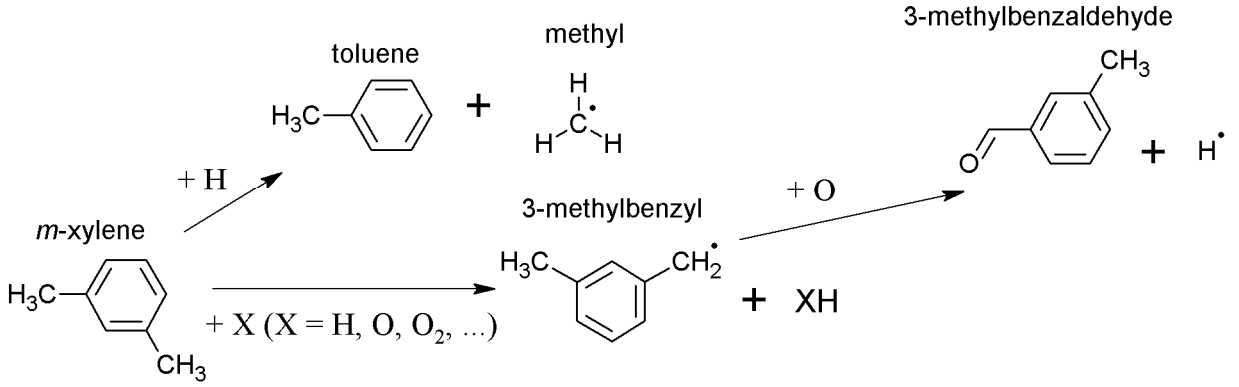

Figure 12: Key branching pathways of m-xylene oxidation.

A rate-of-production (ROP) analysis was conducted for the evaluation of the Ranzi et al. (2007) model tested under the PFR experimental conditions. As noted, the model was run for a mixture of 77% n-dodecane / 23% xylene. The model predicted that the major species produced from the xylene were phenol and cyclopentadiene. An ROP analysis for the xylene was conducted at 700 K. Additionally, the ROP's for each reaction producing a major aromatic species at 120 ms residence time (40 cm along the reaction tube) were identified. The reaction with the maximum absolute ROP was identified. All reactions that contributed at least 5% of the maximum ROP (either forward or reverse) were considered significant for analysis. Figure 13 shows the results of the analysis, detailing the key reaction pathways. While the production of the xylyl radical was predicted, the stable product from later reactions, phenol, was not observed in the experiments. Nevertheless, the lumping of the xylene isomers in the model was verified for lower temperatures. At higher temperatures, the lumping of the xylenes appears reasonable, as the reactivity differences, while noticeable, are not significant.

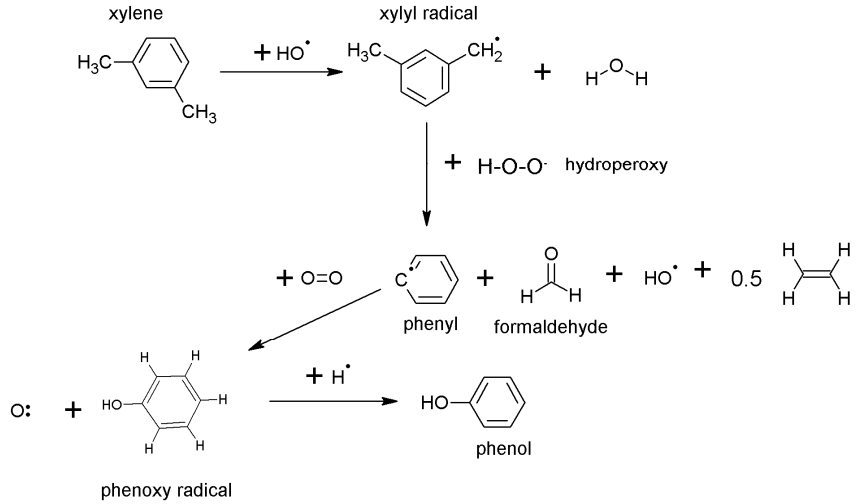

Figure 13: Low temperature branching pathway of xylene based on Ranzi et al. (2007) model.

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